

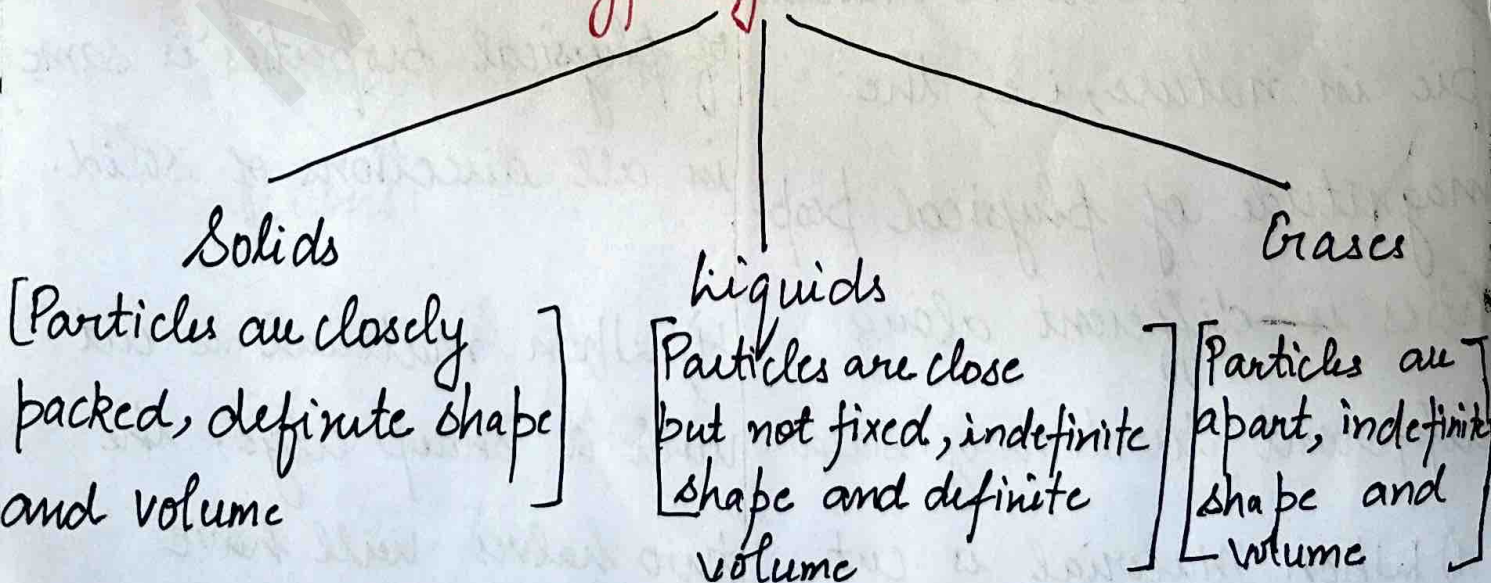
Crystal Structure

①

Topics covered

- Types of Matter
- Types of solids (Crystalline and Amorphous)
- Crystal Structure, Bravais lattices, Co-ordination number
- Simple Cubic (SC), Body Centered Cubic (BCC), Face centered Cubic (FCC)
- Atomic packing fraction
- Miller Indices
- Interplanar Spacing
- Density of states

Types of Matter



→ Plasma is considered as 4th state of matter.

⇒ Solids are further classified into two -

- 1) Crystalline
- 2) Amorphous

① Difference between crystalline and amorphous -

Crystalline

1) A crystalline solid is a material whose constituents are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions.

2) These materials have a sharp melting point.

3) These materials are anisotropic in nature, i.e., the magnitude of physical properties is different along different directions of solid.

4) When material is cut with a sharp edge, the two halves have a smooth surface.

Amorphous

1) An amorphous solid is a material that lacks the long range order that is characteristic of a crystal.

2) These materials do not have a sharp melting

3) These materials are isotropic in nature, i.e., the magnitude of physical properties is same in all directions of solid.

4) When material is cut with a sharp edge, the two halves will have irregular surfaces.

5) They are rigid solids and applying mild forces will not distort its shape.

Eg: Iron, Diamond

5) These materials are ^{not} rigid, so mild forces may change the shape.

Eg: Window glass, Rubber

→ Crystal structure is the structure of crystalline solids.

→ Crystallography is the branch of science that deals with discerning the arrangement and bonding of atoms in crystalline solids and with the geometric structure of crystal lattices.

→ $\text{Crystal structure} = \text{Space lattice} + \text{Basis}$

A space lattice is a three-dimensional, infinite array of imaginary points, repeated periodically in all directions.

Basis is a group of one or more atoms associated with each lattice point of a space lattice, such that when the basis is translated by a lattice vector, the entire crystal structure is reproduced.

Unit Cell

The smallest volume element of a crystal lattice that retains the full symmetry and structural information of the crystal. It is the smallest repeating structure.

- Unit Cell is of two types.
- Primitive and non-primitive.

In an unit cell, when effective number of atoms is 1, it is said to be primitive unit cell.

Ex: Simple Cubic

In an unit cell, when effective number of atoms is more than 1, it is said to be non-primitive unit cell. Ex: Face centered Cubic and Body centered Cubic

FAQ's

① Is there any term like polycrystalline?

It is a solid material composed of large number of small crystals, each having different orientations.

Ex: Copper.

② Predict the unit cell of NaCl?

Face Centered Cubic (FCC)

→ In order to define space lattices, there are 6 important lattice parameters. These 6 are -

- Length of axis along x, y, z
 - Angle between y and z axis - (α)
 - Angle between x and z axis - (β)
 - Angle between x and y axis - (γ)
- Total (6) lattice parameters.

→ These 6 lattice parameters give rise to 7 crystal systems.

<u>Sl. no.</u>	<u>Lattice parameters</u>	<u>Crystal Structure</u>
1.	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	Cubic
2.	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	Tetragonal
3.	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	Orthorhombic
4.	$a \neq b \neq c, \alpha = \beta = 90^\circ, \gamma \neq 90^\circ$	Monoclinic
5.	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	Triclinic
6.	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	Rhombohedral (Trigonal)
7.	$a = b \neq c, \alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Hexagonal.

Bravais lattice

In the 7 crystal systems, the placement of atoms leads to (14) Bravais lattices.

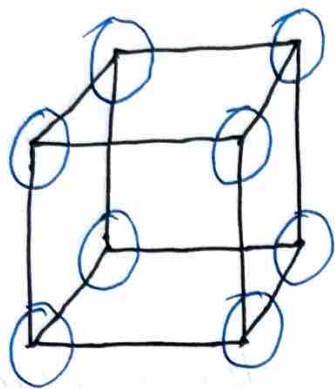
→ Cubic ($a = b = c$, $\alpha = \beta = \gamma = 90^\circ$)

For cubic structure, we have 3 possibilities of atom placement.

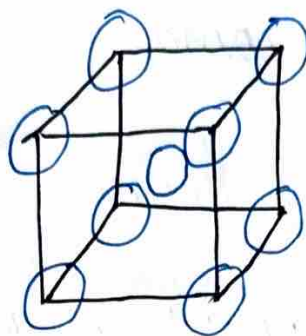
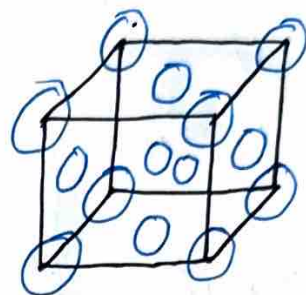
① In a cubic structure, when atoms are placed on all eight corners, it is said to be Simple Cubic structure or primitive structure. (SC)

② In a cubic structure, when atoms are placed on all eight corners and 1 atom is inside the body of cube, it is said to be Body Centered Cubic (BCC).

③ In a cubic structure, when atoms are placed ~~inside the~~ on all eight corners and at all 6 faces of cube, it is said to be Face centered cubic structure. (FCC)



Simple Cubic (SC)

BCCFCC

- Effective number of atoms in Simple Cubic is (1). [Also called Primitive Cell]
- Effective number of atoms in Body Centered Cubic is (2).
- Effective number of atoms in Face Centered Cubic is (4).

Same way different crystal systems can have different arrangement of atoms.

- ② Tetragonal: At corners, Body Centered.
- ③ Orthorhombic: At corners, Body Centered, Face centered, Base Centered [At corners + 2Base]
- ④ Hexagonal: Only one arrangement.

⑤ Monoclinic: At corners, Base Centred

⑥ Trigonal: Only corners

⑦ Triclinic: Only corners

→ Together these arrangements make 14 Bravais lattices.

Coordination Number

The number of nearest neighboring atoms or ions directly surrounding a central atom or ion within a crystal system is the co-ordination number.

Co-ordination number for different crystal systems—

→ Simple Cubic (SC) — 6

→ Body Centred Cubic (BCC) — 8

→ Face Centred Cubic (FCC) — 12

Atomic Packing Fraction

It is the fraction of total volume of a unit cell that is occupied by atoms.

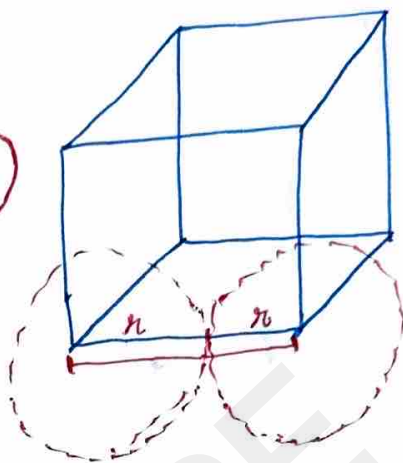
$$APF = \frac{\text{Volume of atoms in unit cell}}{\text{Volume of unit cell}}$$

① APF for Simple Cubic (SC)

⑤

We have a cube of side 'a'.

For a cubic structure, the total volume of a cube is a^3



Now, let's assume the radius of atoms is r , so volume of 1 sphere or atom = $\frac{4}{3} \pi r^3$

Total volume of all atoms = no. of effective atoms $\times \frac{4}{3} \pi r^3$

No. of effective atoms in SC = 1

Relationship between a and r is $a = 2r$

$$\text{APF} = \frac{\text{no. of effective atoms} \times \frac{4}{3} \pi r^3}{a^3}$$

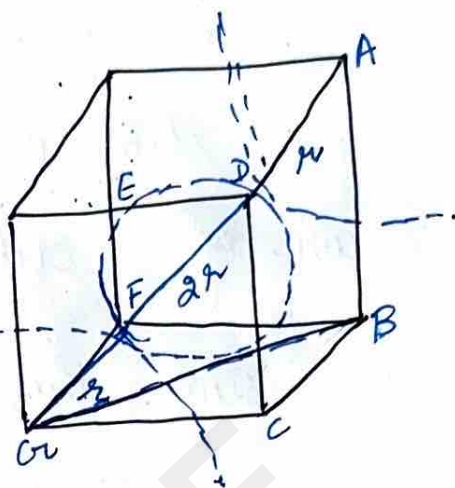
Substituting $a = 2r$

$$= \frac{1 \times \frac{4}{3} \pi r^3}{(2r)^3} = 0.52$$

So packing fraction for SC is 52%.

② Body Centered Cubic (BCC)

In BCC, the no. of effective atoms = 2



$$APF = \frac{\text{no. of effective atoms} \times \frac{4}{3}\pi r^3}{\text{Volume of cube}}$$

Volume of cube

$$= \frac{2 \times \frac{4}{3}\pi r^3}{a^3} \quad \leftarrow (1)$$

Now, we need to find relationship between a and r —

$$\text{In } \triangle GBC, (GB)^2 = (GC)^2 + (BC)^2$$

$$GC = BC = a \text{ (side of cube)}$$

$$\Rightarrow (GB)^2 = a^2 + a^2 = 2a^2 \quad \leftarrow (2)$$

$$\text{In } \triangle AGB, (AG)^2 = (GB)^2 + (AB)^2$$

$AB = a$ (side of cube) and substituting value of $(GB)^2$ from (2)

$$\Rightarrow (AG)^2 = 2a^2 + a^2 = 3a^2$$

From figure $AC = 4r \rightarrow$

(6)

$$16r^2 = 3a^2$$

$$\Rightarrow \frac{16r^2}{3} = a^2$$

$$\Rightarrow \boxed{\frac{4}{\sqrt{3}} r = a}$$

Substituting value of a in ①

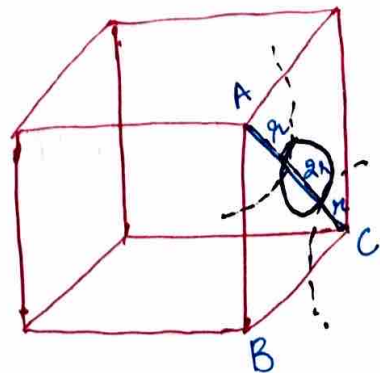
$$APF = \frac{2 \times \frac{4}{3} \pi r^3}{\left(\frac{4}{\sqrt{3}} r\right)^3} = 0.68$$

So packing fraction for BCC is 68%.

③ Face Centered Cubic (FCC)

In FCC, the number of effective atoms is 4

$$APF = \frac{\text{no. of effective atoms} \times \frac{4}{3} \pi r^3}{\text{Total Volume}}$$



$$= \frac{4 \times \frac{4}{3} \pi r^3}{a^3} \quad \leftarrow (3)$$

Now we need to find relationship between r and a ,
(r is radius of atom)
In $\triangle ABC$,

$$(AC)^2 = (AB)^2 + (BC)^2$$

$$(4r)^2 = a^2 + a^2 \quad [AB = BC = a \text{ is side of cube}]$$

$$16r^2 = 2a^2$$

$$\Rightarrow \boxed{\frac{4r}{\sqrt{2}} = a} \quad \leftarrow (4)$$

Substituting (4) in (3) $\rightarrow$

$$APF = \frac{4 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = 0.74$$

So atomic fraction for FCC is **74%**

Interplanar Spacing

⑦

It is the perpendicular distance between two adjacent parallel crystallographic planes having miller indices $(h k l)$. It is denoted by (d_{hkl})

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

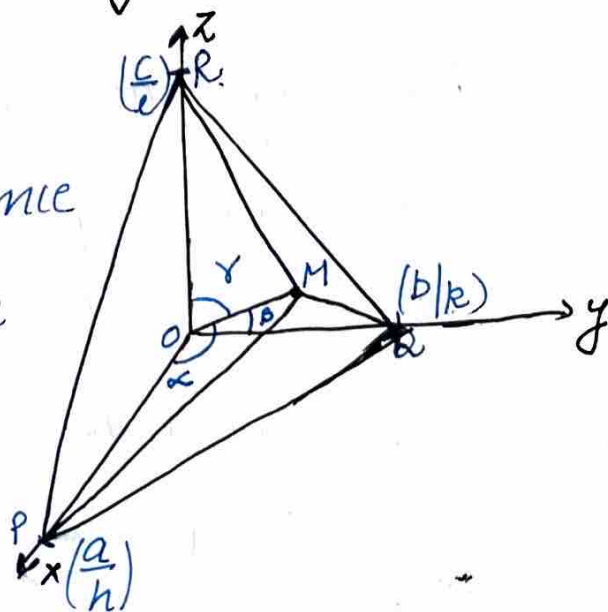
where a, b, c are lattice parameters or lattice constants.
For a cube, $a = b = c$, we get -

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Derivation of interplanar spacing

We are given a plane PQR,
OM is the perpendicular distance
of this plane, from another
plane placed at origin O.

So $OM = d$ (interplanar spacing)



Now, the miller indices for given PQR plane is $(h\ k\ l)$. So the x-intercept = $\frac{a}{h}$

$$y\text{-intercept} = \frac{b}{k}$$

$$\text{and } z\text{-intercept} = \frac{c}{l}$$

where a, b, c are lattice parameters.

In $\triangle OMP$ (right angled at $\angle OMP$)

$$\cos \alpha = \frac{OM}{OP} = \frac{dh}{a} \quad \text{--- (1) [OP is x-intercept]}$$

In $\triangle OMQ$ (right angled at $\angle OMQ$)

$$\cos \beta = \frac{OM}{OQ} = \frac{dk}{b} \quad \text{--- (2) [OQ is y-intercept]}$$

In $\triangle OMR$ (right angled at $\angle OMR$)

$$\cos \gamma = \frac{OM}{OR} = \frac{dl}{c} \quad \text{--- (3)}$$

By rule of direction cosines, $\rightarrow$

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1$$

substituting from 1, 2 and 3 $\rightarrow$

$$\frac{d^2 h^2}{a^2} + \frac{d^2 k^2}{b^2} + \frac{d^2 l^2}{c^2} = 1 \quad (8)$$

$$\Rightarrow d^2 \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right] = 1$$

$$\Rightarrow d = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

For a cube, $a = b = c \rightarrow$

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$\textcircled{1} \text{ For orthorhombic } a \neq b \neq c$$

$$d = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

$$\textcircled{2} \text{ For Tetragonal } a = b \neq c$$

$$d = \frac{1}{\sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}}$$

Miller Indices

- Miller indices are used to specify directions and planes.
- The number of indices will match with dimension of lattice.
- Miller indices are represented as $(h \ k \ l)$
- Family of miller indices is given by $\{h \ k \ l\}$
- Miller indices can never be infinity.

- Miller indices is always an integer (can never be fraction)
- Miller plane can never be at infinity origin.
- Whenever any axis is parallel to a plane, intercept is ∞ .

How to find Miller Indices?

- ① Write the intercepts
- ② Take the reciprocal of intercepts.
- ③ Clear fractions.

Three type of numericals

- ① Type 1: Intercepts are given and find miller indices
- ② Type 2: Miller plane is given and find indices.
- ③ Type 3: Draw the miller planes.

Type 1: Intercepts are given

Examples

- ① A miller plane has intercepts $2a$, $3b$ and c along crystallographic axes. Determine miller indices.

	x	y	z
Intercepts	$2a$	$3b$	c
Reciprocal	$\frac{1}{2}$	$\frac{1}{3}$	1

Clear fraction - $\frac{1 \times 6}{2} \quad \frac{1 \times 6}{3} \quad 1$ [By taking LCM] ⁽⁹⁾

$\Rightarrow (3 \quad 2 \quad 1)$ are miller indices.

② Given intercepts $(1, \infty, \infty)$

Intercepts	x	y	z
	1	∞	∞
Reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{\infty}$

$(1 \quad 0 \quad 0)$ are miller indices

③ Given intercepts $(2a, 3b, 4c)$, where a, b and c are ~~inter~~ lattice constants of unit plane.

Intercepts	x	y	z
	$2a$	$3b$	$4c$
Reciprocal	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$

Clear fraction $\frac{1 \times 12}{2} \quad \frac{1 \times 12}{3} \quad \frac{1 \times 12}{4}$

$(6 \quad 4 \quad 3)$

④ Given intercepts $(-1, -2, 3)$

Intercepts	x	y	z
	-1	-2	3

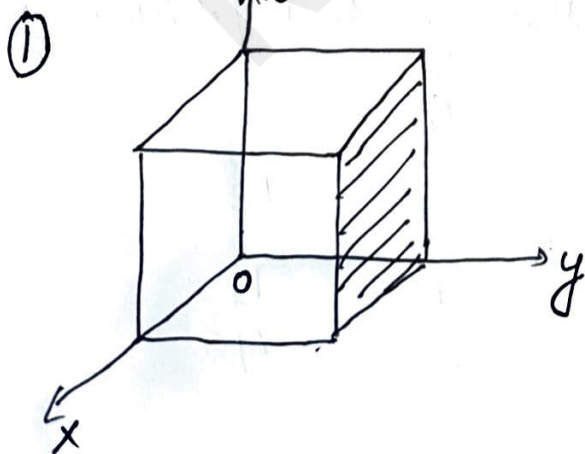
Reciprocal	$-\frac{1}{1}$	$-\frac{1}{2}$	$+\frac{1}{3}$
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Remove fraction	$\frac{-1 \times 6}{1}$	$\frac{-1 \times 6}{2}$	$+\frac{1 \times 6}{3}$
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$$\Rightarrow (\bar{6} \quad \bar{3} \quad 2)$$

[Note: For negative intercepts, miller planes are represented as bar (-)]

Type 2: For given plane, find indices:

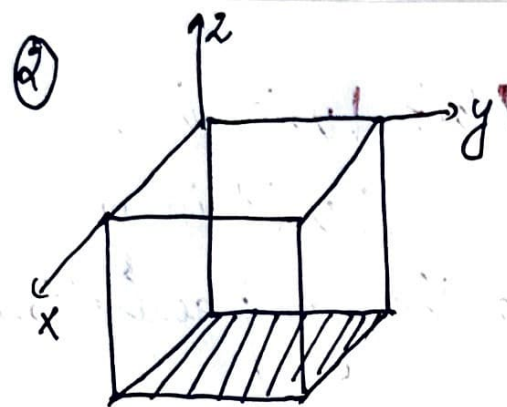


Intercepts	x	y	z
	∞	1	∞

Reciprocal	$\frac{1}{\infty}$	$\frac{1}{1}$	$\frac{1}{\infty}$
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$$\text{Indices } (0 \ 1 \ 0)$$

[From origin to x-axes (plane is not found) so, intercept is ∞ , same for z]



(Whenever plane is at usual origin, change the origin because plane cannot be at origin)

Intercepts .	x	y	z
	∞	∞	-1
Reciprocal	$\frac{1}{\infty}$	$\frac{1}{\infty}$	$-\frac{1}{1}$

$$\Rightarrow (0 \ 0 \ 1)$$

Type 3: Draw given miller plane

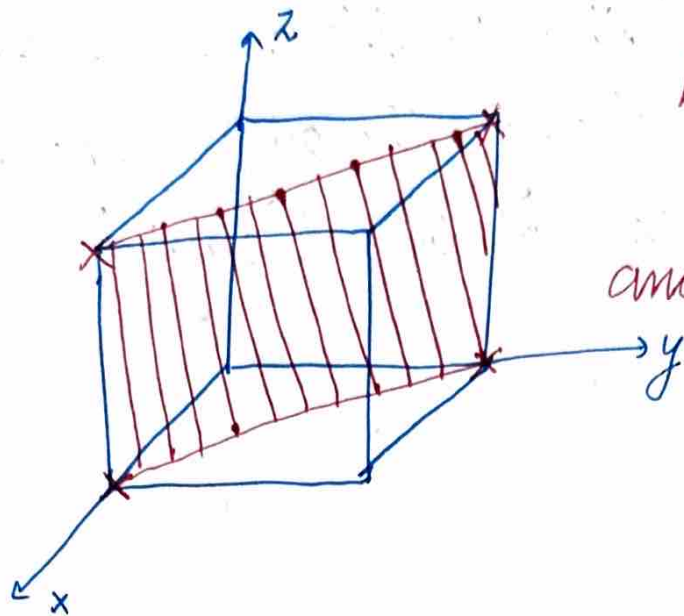
- Mark the intercepts for all directions
- If intercept is ∞ , the plane will be parallel to that axes.
- For negative intercept, shift exactly 1 unit from origin in the negative direction.

Ex: 1: Given miller plane $(1 \ 1 \ 0)$

	x	y	z
Miller Plane	1	1	0

Intercept	1	1	∞
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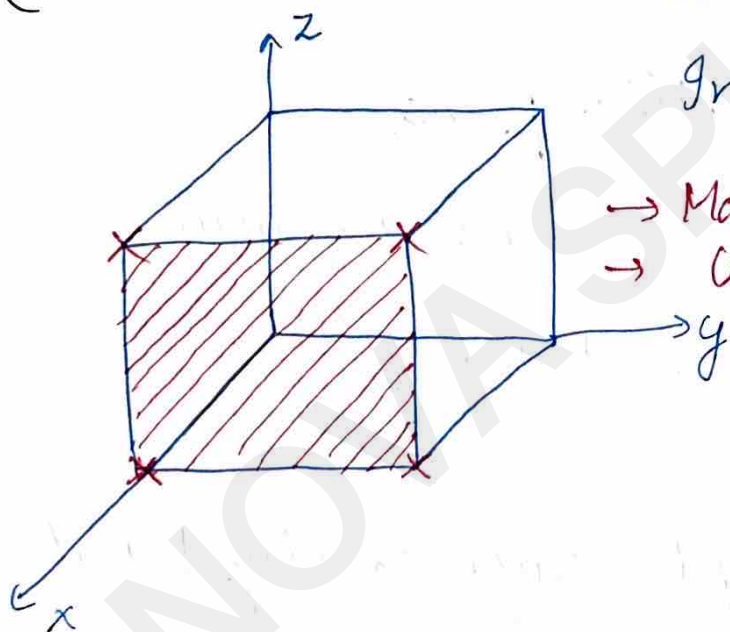
[Reciprocal of Miller Indices]



Mark 1 unit in x
1 unit in y
and then go parallel to z

② $(1\ 0\ 0)$

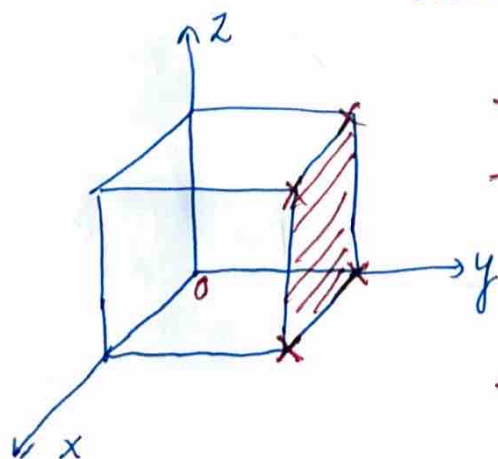
	x	y	z
Miller Indices	1	0	0
Intercept	1	∞	∞



→ Mark 1 unit in x
→ Go parallel to y
→ From those 2 points, go parallel to z

③ $(0\ 1\ 0)$

	x	y	z
Miller indices	0	1	0
Intercept	∞	1	∞



→ Mark 1 point in y
→ Go parallel to x from that point
→ Go parallel to z .

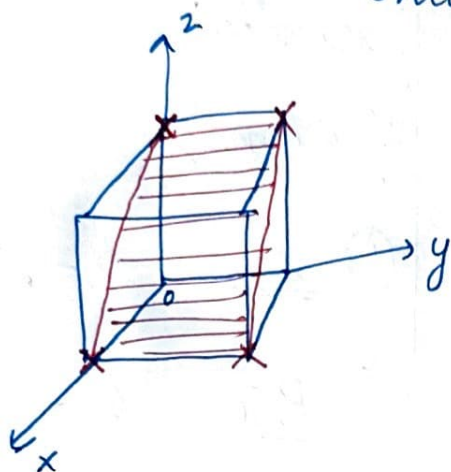
④ (101)

Miller Indices

x y z (11)

Intercepts

1 ∞ 1



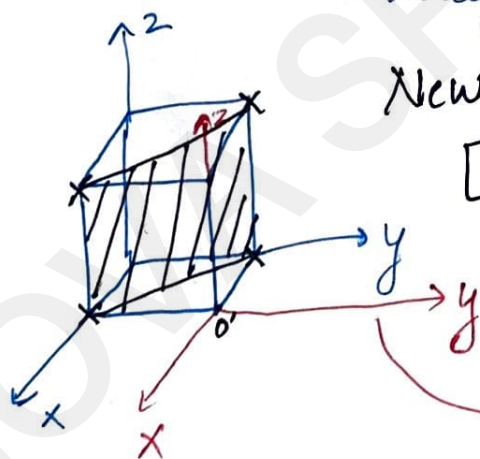
⑤ (1̄1̄0)

Miller Indices

x y z

Intercepts

-1 -1 ∞



New origin in at o'
[1 unit in x and 1 unit in y for -ve intercept]

→ New co-ordinates.

Density for cubic crystal

$$\text{Density} = \frac{nM}{N_A a^3}$$

no. of effective atoms

Molecular or Atomic weight

side of cube or lattice parameter

Avogadro's number (6.022×10^{23})

Effective no. of atoms (n)

① SC = 1

② BCC = 2

③ FCC = 4

Relationship between a (side of cube or lattice parameter) and r (radius of atoms):

① SC $a = 2r$

② BCC $a = \frac{4r}{\sqrt{3}}$

③ FCC $a = \frac{4r}{\sqrt{2}}$